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Free-Standing 2D Silicon Nanocrystals Stabilized With Perfluorophenyl Ligands: Experiment and Ab Initio Research

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Abstract. Silicon (Si) is currently the basis of most of nanodevice technology, therefore ultrathin materials based on Si have the great advantage of easy integration into existing circuitry. First flat silicon nanoparticles have been obtained with perfluorophenyl (PFPh) ligand coating. The size of these particles varied from 15 to 50 nm. Their thickness evaluated with the atomic force microscopy was about 3.3 nm. Based on *ab initio* DFT calculations we investigate the geometries and electronic structures of free-standing PFPh-stabilized 2D silicon in order to see if such systems have promising electronic and optical properties. We also examined the effect of doping PFPh-stabilized 2D silicon by the Mn atoms.

Introduction

Up to now silicon in the nanocrystalline state was prepared as quantum dots or nanowires, but in the last 3-4 years there appeared an interest to 2D structures produced on supports or in colloidal media. Recently, monoatomic silicon layers were extracted from the $CaSi_2$ crystals as they were and then stabilized by phenyl groups) [1] or hexyl groups [2]. The $CaSi_2$ crystals contain graphene-like layers consisting of Si atoms and these layers are interlaced by Ca atoms. In the present work we describe assembling of the separate Si atoms into flat nanoparticles in colloid. Existing facts show that graphene-like monoatomic layers of silicon cannot be obtained without supports, that is all 2D silicon structures prepared in colloidal media should have a certain thickness [3]. The 2D nanocrystals (nc) of semiconductors of AIIBVI type have been obtained, and it was shown that the ligands play an important role in the nc synthesis [4]. Using synthetic procedure in solution (bottom-up) [5], we have obtained for the first time the sandwich-like flat nc-Si as free-standing crystals with the thickness less than 10 nm.

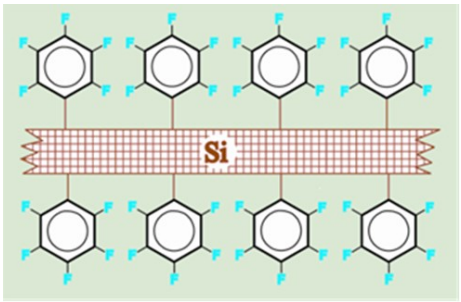

Fig. 1. Flat silicon nanocrystal stabilized by the perfluorophenyl ligands.

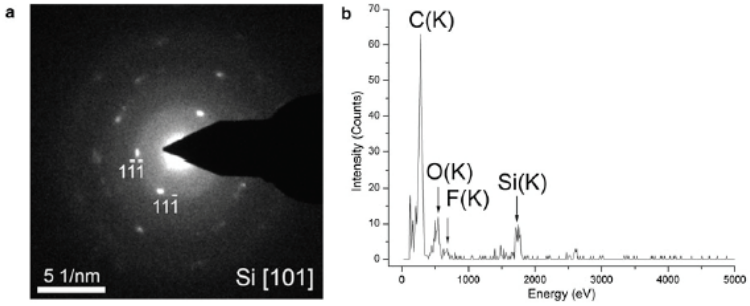

Fig. 2. DP (a) and EDX spectrum (b) of the flat Si nanocrystals.

Experimental section

We performed a series of syntheses of nc-Si covered by phenyl, butyl, perfluorobutyl, and carbene ligands [6-8] in different organic solvents, and in all of them only isotropic nanoparticles (quantum dots) were obtained. But when we used perfluorophenyl radical we obtained quite different result, namely we had both quantum dots and 2D structures at the same time. Briefly, 2D silicon nanocrystals were obtained by reduction of $SiBr_4$ ($SiCl_4$) with potassium in 1,2-dimethoxyethane, and the remaining bromide ligands on the nc-Si surface were replaced by perfluorophenyl groups by adding the nc-Si dispersion to the 20% excess of perfluorophenyllithium prepared from bromopentafluorobenzene and lithium amalgam. Typical examples of detailed synthetic procedure and characterization methods are given in [5]. We have concluded that lamellar nanocrystals (Fig.3) are possibly formed at the stage of replacement of the bromide ligands by perfluorophenyl groups on the surface of small silicon nanoparticles and are the products of aggregation of these silicon nanoparticles into flat plates. In our opinion, growth of the plates is caused by C--F-specific interactions between the ligands, which results in formation of layers of the perfluorophenyl ligands due to their self-assembly in fluorophobic media. The mechanism of the perfluorophenyl ligand self-assembly is related to specific interactions. The centre of perfluorophenyl ring has a considerable positive charge because of attraction of electrons by fluorine atoms from π-orbibals of the perfluorophenyl ring, so the perfluorophenyl rings can interact with each other by a contact between the electronegative fluorine atom and the electropositive centre of perfluorinated ring [5]. This mechanism was observed in the edge-to-face (T-shape) structure of hexafluorobenzene [5].

Obtained crystals were studied by FTIR, TEM, AFM, EDX, XPS and PL spectroscopy. Along with halo-like diffraction patterns (DP) from spherical particles, the spot diffraction patterns were observed for flat Si-nanoparticles (Fig. 2a) which have the crystalline structure. The energy dispersive X-ray (EDX) analysis reveals the presence of C, Si, O and a trace amount of F (Fig. 2b). High-resolution TEM images of crystalline flat particles are shown in Fig. 3.

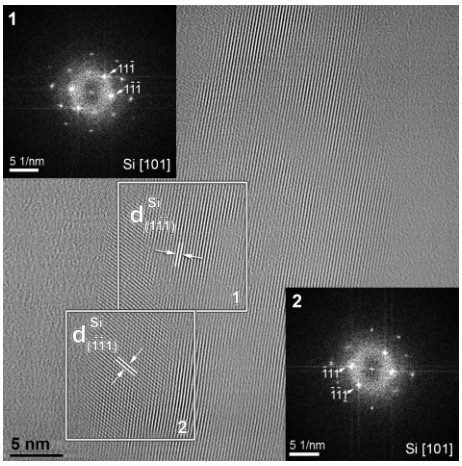

Fig. 3. Filtered HRTEM image of a large flat Si particle. Insets: diffractograms of isolated squared areas corresponding to [101] zone.

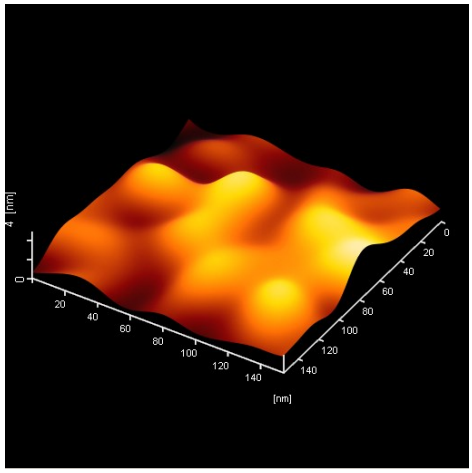

Fig. 4. Analysis of nc-Si lamellae by AFM (nanoprofilometry data on the morphology of the nc-Si surface).

The thickness of flat nanocrystals was evaluated by Atomic Force Microscopy (AFM) (Fig. 4): it is close to 3.3 nm in average, and areas of uniform thickness gained 30 nm on the support substrate. The 2D silicon nanocrystals as large as those presented in Fig. 3, containing ~ 10^5 Si atoms, can be doped for the *p-n* junctions formation in contrast to quantum dots in which the number of silicon atoms is ~1000 whereas one boron or phosphorus dopant atom should be per 10^4 silicon atom.

Method of calculation and DFT results

Ab initio calculations for Si-PFPh were performed by using the APW+lo method as implemented in WIEN2k code [9]. The exchange-correlation effects were described within the GGA approximation [10]. DFT calculations were made within the supercell of Si-PFPh, containing 78 atoms, i.e. 6Si+6H+36C+30F, inside the cubic box of about 20 Å (see Fig. 5). Converged results were obtained at the cut-off energy for the interstitial plane-wave expansion of 354 eV. Relaxations of all atomic positions were included in our calculations until the Hellmann-Feynman forces at each site were less than 2 meV/Å. As is seen from the calculated band structure and density of states (DOS) (Fig. 6), the system shows the direct band gap of 3.21 eV, which demonstrates a significant effect of molecular functionalization by PFPh ligands on Si-PFPh electronic structure (cf. $E_g \sim 2$ eV in phenyl- and hexyl-modified silicon nanosheets [11, 12]). The *ab initio* simulation also shows that the PFPh ligands slightly rotate and tilt on the Si buckled nanolayer.

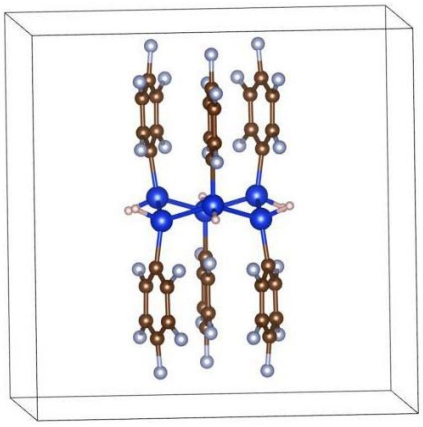

Fig. 5. Structure of the relaxed buckled PFPh, monolayer Si-PFPh. Blue balls are Si, of Si, brown – C, grey – F and pink – H.

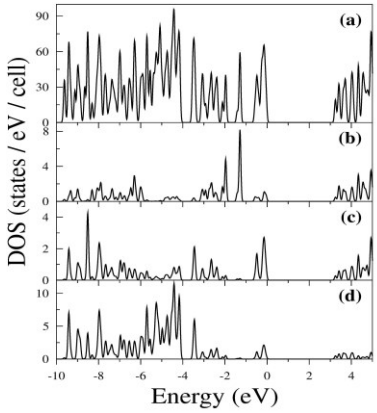

Fig. 6. (a) Total electronic density of states of Si-(b), (c), and (d) sum of orbital- decomposed DOS C and F atoms, respectively. The zero of energy is aligned to the highest occupied level.

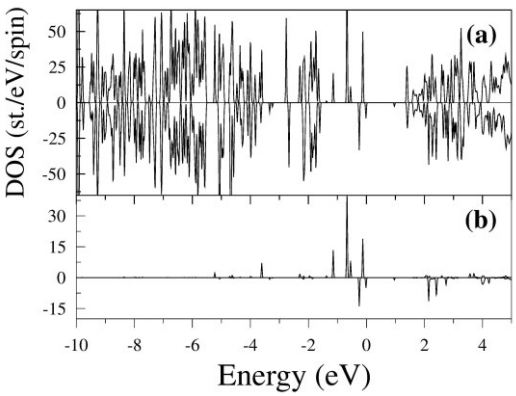

Fig. 7. (a) Total electronic DOS of Si-PFPh:Mn, Si-PFPh:Mn, b) 3d states of orbital-decomposed DOS of the Mn.

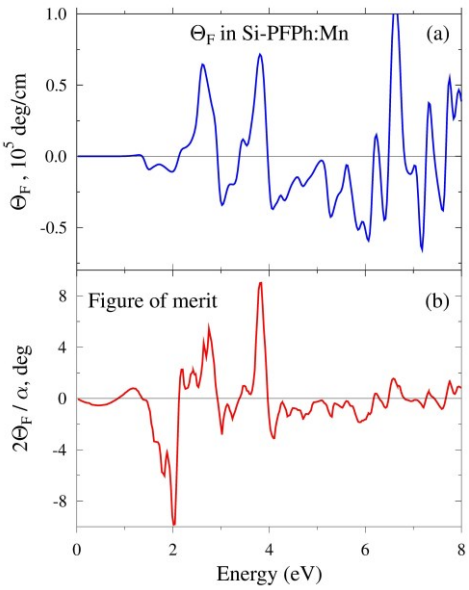

Fig. 8. (a) Calculated Faraday rotation $\Theta_F(\omega)$ for Si-PFPh:Mn, and (b) corresponding figure of merit $F(\omega)$.

We also examined the effect of doping PFPh-stabilized 2D-silicon by the Mn interstitial placed in the centre of buckled hexagonal ring of Si atoms (Si-PFPh:Mn). The Mn dopant shrinks the native (Si-PFPh) band gap to a value of 0.96 eV due to appearing 3d-states of Mn inside the native gap (Fig. 7). Total energy difference between ferromagnetic (FM) and non-magnetic (NM) states reveals very large energy gain of FM state over NM one (~0.76 eV/cell). Magnetic state is characterized by 3 μ_B/Mn (5 spin up and 2 spin down Mn 3d-states). Note that our preliminary calculations on the doping of Si-PFPh by another interstitials, e.g. Cr, Fe, Co and Ni, have resulted in the following magnetic moments: 4 μ_B/Cr, 2 μ_B/Fe, 1 μ_B/Co and 0 μ_B/Ni, respectively.

The magneto-optical (MO) Faraday effect was calculated in the framework of the relativistic WIEN2k code [9]. By use of calculated dielectric tensor elements, we derived an energy dependence of the specific Faraday rotation Θ_F (Fig. 8 (a)), optical absorption α, and the MO figure of merit $F=2\Theta_F/\alpha$ (Fig. 8 (b)). We have calculated F as a function of energy for the interband transitions in Si-PFPh:Mn and show that F achieves a maximum value of 10^o in a visible part of the spectrum of radiation of about 2-4 eV (cf. F_{max}~3^o in iron at $\hbar\omega$~1.3 eV).

Acknowledgements

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References

[1] Y. Sugiyama, H. Okamoto, T. Mitsuoka et al., Synthesis and Optical Properties of Monolayer Organosilicon Nanosheets, J. Am. Chem. Soc., 132 (2010) 5946-5947.

[2] H. Nakano, M. Nakano, K. Nakanishi et al., Preparation of alkylmodified silicon nanosheets by hydrosilylation of layered polysilane (Si6H6), J. Am. Chem. Soc., 134 (2012) 5452–5455.

[3] R. Hoffmann, Small but Strong Lessons from Chemistry for Nanoscience, Angew. Chem. Int. Ed., 52 (2013) 93–103.

[4] Wen X-D, Hoffmann R, Ashcroft N.W., Two-Dimensional CdSe Nanosheets and their Interaction with Stabilizing Ligands, Adv. Mater., 25 (2013) 261–266.

[5] A.S. Orekhov, S.V. Savilov, V.N. Zakharov et al., The isolated flat silicon nanocrystals (2D structures) stabilized with perfluorophenyl ligands, J. Nanopart. Res., 16 (2014) 2190-2197, and references therein.

[6] L.A. Aslanov, V.N. Zakharov, M.A. Zakharov et al., Stabilization of silicon nanoparticles by carbenes, Russ. J. Coord. Chem., Pleiades Publishing Ltd., 36 (2010) 330 -332.

[7] L.A. Aslanov, V.N. Zakharov, A.V. Pavlikov et al., Synthesis and Properties of Nanosilicon Stabilized by Butyl and Perfluorobutyl Ligands, Russ J. Coord. Chem., Pleiades Publishing Ltd., 39 (2013) 427-431.

[8] A. Kamyshny, V.N. Zakharov, M.A. Zakharov et al., Photoluminescent Silicon Nanocrystals Stabilized by Ionic Liquid, J. Nanopart. Res. 13 (2011) 1971-1978.

[9] P. Blaha, K. Schwarz, G.K.H. Madsen et al. Wien2k, An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties (K. Schwarz, Techn. Universitat Wien, Austria, 2001).

[10] J.P. Perdew, S. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77 (1996) 3865-3868.

[11] M.J.S. Spencer, M.R. Bassett, T. Morishita et al., Interactions between stacked layers of phenyl-modified silicene, New Journal of Physics 15 (2013) 125018-1—125018-12, and references therein.

[12] Feng Li, Ruifeng Lu, Qiushi Yao et al., Geometric and Electronic Structures as well as Thermodynamic stability of Hexyl-Modified Silicon Nanosheet, Journal of Physical Chemistry C 117 (2013) 13283−13288.